

Thermal Decomposition of New and Aged LX-04 and PBX 9501

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THERMAL DECOMPOSITION OF NEW AND AGED LX-04 AND PBX 9501

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ABSTRACT

One-Dimensional-Time-To-Explosion (ODTX) experiments were conducted to study the thermal decomposition of aged LX-04, aged PBX 9501, HMX class 1 and class 2, Estane and Estane/BDNPA-F (PBX 9501 plasticized-binder) materials. The tests involved heating 12.7 mm diameter spherical samples in pre-heated aluminum anvils until explosion. The times to explosion at different heating temperatures were compared to historical data on new LX-04 and PBX 9501 compounds to study any changes to their thermal stability. New and aged LX-04 showed comparable decomposition kinetics. The data for aged PBX 9501 showed slightly longer explosion times at equivalent temperatures. Analysis of the error in time measurement is limited and complicated by several experimental factors but the small time change appears to be experimentally significant.

The thermal decomposition of these PBXs were modeled using a coupled thermal and heat transport code (chemical TOPAZ) using separate kinetics for HMX and binder decomposition. Separate decomposition models were developed for HMX and the reactive PBX 9501 binder component (1:1 Estane:BDNPA/F) based on the measured explosion times. Thermal aging models can describe longer explosion times by the loss of plasticizer-binder constituent which was more thermally reactive.

INTRODUCTION

An integrated One-Dimensional-Time-To-Explosion (ODTX) experimental and chemical kinetic decomposition modeling effort was undertaken to determine whether stockpile aged HMX-based plastic bonded explosives, such as LX-04 and PBX 9501, are more thermally sensitive than new materials. The ODTX data on aged specimens were obtained and compared directly to historical data that were available on these materials (1,2). Recent experiments also included tests on pure HMX (both classes 1 and 2) and binder components used in both these composites. The results are useful for developing kinetic models for pure HMX and the composite binder. The upgraded HMX model incorporates kinetics for the β - δ HMX phase transition (3), which precedes the exothermic decomposition.

ODTX experiments have been used extensively to study the thermal explosions of a wide variety of high explosives (HE) including many HMX-based formulations (1-2,4-5). The test involves heating a 12.7 mm-diameter HE sphere confined in two pre-heated constant-temperature aluminum anvils until the material explodes. The confinement is set at 150 MPa. The time to explosion is the elapsed time between the sample insertion (and anvil closure) and the rupture of containment. The time to explosion as a function of the temperature provides useful kinetic information on the material decomposition.

EXPERIMENTAL

All experiments were conducted on an ODTX apparatus that was developed by Catalano and co-workers (1). This work and subsequent data were conducted on relatively new LX-04 and PBX 9501 materials. A short description of the experiment and the apparatus is presented below. Additional details are presented elsewhere (1-2,4).

The main components of the test are two cylindrical aluminum anvils (75-mm diameter x 50 mm long, 6061 T6 Al). Each anvil contains a 12.7 mm-diameter hemispherical cavity and a 18.5 mm-diameter circular groove with a knife-edge bottom to accommodate a copper O-ring seal (Vacuum Products Corp., GK-075). A circular copper ring clamped between the two knife-edges provides a gas-tight seal when two anvils are pressed together. The upper anvil is mounted to the piston surface of a hydraulic piston (16-ton double-acting hydraulic cylinder, RD-166, Enerpac). The standard operating confinement pressure is 150 MPa. The confinement pressure is calculated based on the cross-sectional area confined by the knife-edge. The two anvils are heated by two 1000 W heating cups. The anvil temperature is controlled by a thermocouple inserted in an aluminum disc placed between the two anvils. The explosion is timed acoustically by a microphone and an analog timer. The system is semi automatic and the test is conducted remotely.

Sample preparation – Due to available technology and nature of the stock materials, the ODTX spheres for various series were prepared in different ways. Historical samples (i.e., new LX-04 and PBX 9501) were die-pressed into hemispheres and then glued together prior to testing. Recent aged LX-04 and PBX 9501 were available as 15.8 mm-diameter right cylinders which were cored from a isostatically pressed hemisphere. They were then machined directly into spheres for testing. Estane samples were pressed to shape in a spherical die without heating. Estane/BDNPA-F (50/50) compound was hand rolled into partially spherical specimens because it did not press well. Relevant history and processing conditions for various materials are summarized in Table 1.

Table 1. History and properties of ODTX samples

	ODTX date	Sample preparation	Average density*, g/cc
New (historical) LX-04 85 wt% HMX, 15 wt% Viton A	1986	Die-pressed hemi Glued with epoxy	1.865
Aged LX-04	2000	Machined into sphere	1.874
New (historical) PBX 9501 95 wt% HMX, 2.5 wt% Estane, 2.5 wt% BDNPA-F	1981	Die-pressed hemi Glued with epoxy	1.785
Aged PBX 9501	2000	Machine into sphere	1.845
HMX grade B, Class 1 (Hol94M033-024)	2000	Die-pressed into sphere	1.772
HMX grade B, Class 2 (Hol98E243-020)	2000	Die-pressed into sphere	1.730
Estane	2000	Die-pressed into sphere	
50 wt% Estane / 50 wt% BDNPA/F	2000	Hand-rolled into sphere	

*Density derived from average weight divided by sample volume (1.07 cm³)

EXPERIMENTAL RESULTS AND DISCUSSION

The explosion times for HMX class 1, HMX class 2, ‘new’ LX04 (data reported in reference 1) and aged LX-04 as functions of inverse temperatures at 150 MPa confinement are shown in Figure 1. The time-inverse temperature curves consist of several linear regions, indicative of fairly complex decomposition processes. At the lowest temperatures (< 205°C) and longest times, thermal explosions may involve pressure bursts where gaseous reaction products exceeded the confinement pressure and popped the anvils open. Such events produce less noise and less damage to the Al anvils. In the highest temperature regime, accelerated decomposition in region close to the sample surface may cause thermal runaway in only part of the sphere. Such events also cause less damage to the anvils. In contrast, the reactions in the intermediate temperature region where isothermal conditions exist are most violent, yielding deep and large cavities. We have presented and discussed such general trends for several materials (5,6).

The times to explosion are fairly similar for both new and 229-month-old stockpile returned LX-04. In addition to age, several experimental factors are different for these two sets of data such as sample type and time separation between the experiments. The effects of sample type (hemi-glued and full spheres) were tested for a variety of HE samples (such as TNT, PS propellants) and were found to be negligible. The effects of apparatus upgrades, system accuracy and other systematic errors associated with the long time separation between the tests are difficult to assess. Agreement between historical and recent data for several sets of materials (i.e., PBX 9501 below and other materials), however, is good. Selected reproducibility studies with TNT using the old ODTX system tests showed a standard error of 5.5 % (1 standard deviation). Tests with PBX 9501 with the new ODTX unit under more controlled conditions (calibrated resistive thermal devices, uniform sample densities, long pre-soak, etc.) showed significant improvement at 2.5%. In light of these assessments, the results for aged LX-04 specimens here showed comparable explosion times to those for newer materials.

The results for both HMX class 1 and class 2 are also included in Figure 1. This is the first time that pure HMX was measured. The slightly larger explosion times in LX-04 (relative to pure HMX) are attributable to the presence of Viton A binder. The binder phase serves as a heat sink which retards the decomposition. The HMX data tracked those for LX-04 well, suggesting that HMX decomposition dominates LX-04 thermal stability. This is consistent with our assumption in previous works on the thermal behavior of HMX-based formulations containing non-reactive binder such as Viton A. Tarver and Tran discuss in more detail the effects of binder type and binder contents on the thermal behavior of HMX-based formulations in another paper (6).

Figure 2 shows the times to explosion for new and stockpile aged (191 months old) PBX 9501. The data for Estane/BDNPA-F binder specimens are also included. Tests with pure Estane did not show any positive events (no reaction as recorded by the acoustic sensor and post-test anvil inspection). A LLNL-formulated new batch of PBX 9501 was also tested to evaluate the variability of the apparatus. Despite the differences in material variability and 20-year time separation between the tests on two new batches PBX 9501, the agreement is good. The reproducibility of these two sets of data demonstrates the higher limit of the experimental accuracy of this system.

Compared to the historical data (new PBX 9501), the stockpile aged PBX 9501 consistently exhibited slightly longer times to explosion for temperatures above 210°C. The time differences are about 50-100 seconds. They are most easily observed in the region between 245-270°C where the explosion times are between 30 and 200 seconds. The longer explosion times in aged specimens (~ 100 seconds) are significantly larger than expected standard errors (~10 s). These changes, therefore, reflect the slower decomposition kinetics of the aged materials and not test variabilities.

Understanding of the possible changes in the thermal behavior of aged specimens is complicated by the lack of material compositional and detailed processing history. The surveillance data on aged PBX 9501 show a trend that the Estane molecular weight is decreasing with time and that some nitroplasticizer migrates into other components at certain locations. The loss of the nitroplasticizer (NP) content, however, is small and that the NP concentration is within specifications. The effects of Estane decreased molecular weight or lower NP concentration (albeit small) on PBX 9501 decomposition are not understood. Estane/BDNPA-F ODTX data (see Figure 2) clearly showed more reactivity and are expected to influence the thermal behavior of PBX 9501. The thermal effects of this component on the composite explosion times need to be investigated further. The densities of aged materials in recent tests are somewhat higher than those for historical data from earlier work (see Table 1). This density effect and other experimental variables, such as glued hemispheres versus machined isostatically pressed spheres, on the thermal decomposition of PBX 9501 have not been studied. At this point, we can not attribute the measured longer explosion times in aged specimens to any observable changes in material properties.

Reaction violence - The thermal explosions of LX-04 and PBX 9501 are generally among the most violent reactions we have experienced, producing loud events with large sample cavity increase and no residues. The violence of the thermal explosions in ODTX apparatus can be correlated to the increase in the cavity volume. The cavity volume was measured gravimetrically by weighing the amount of soap/water solution that filled the cavity. ODTX experiments are more violent in the intermediate temperature region where reaction conditions are isothermal, resulting in

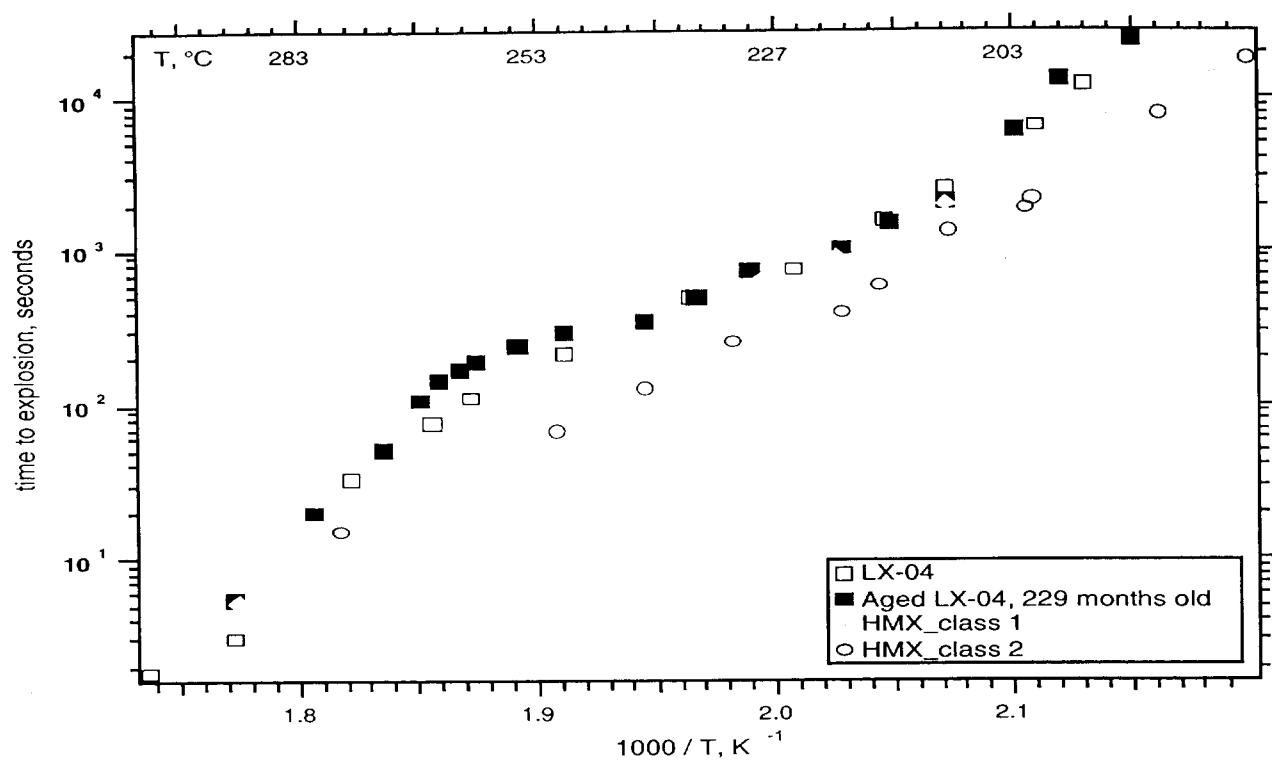


Figure 1. Time to explosion versus inverse temperature for new, aged LX-04 and HMX classes 1 & 2.

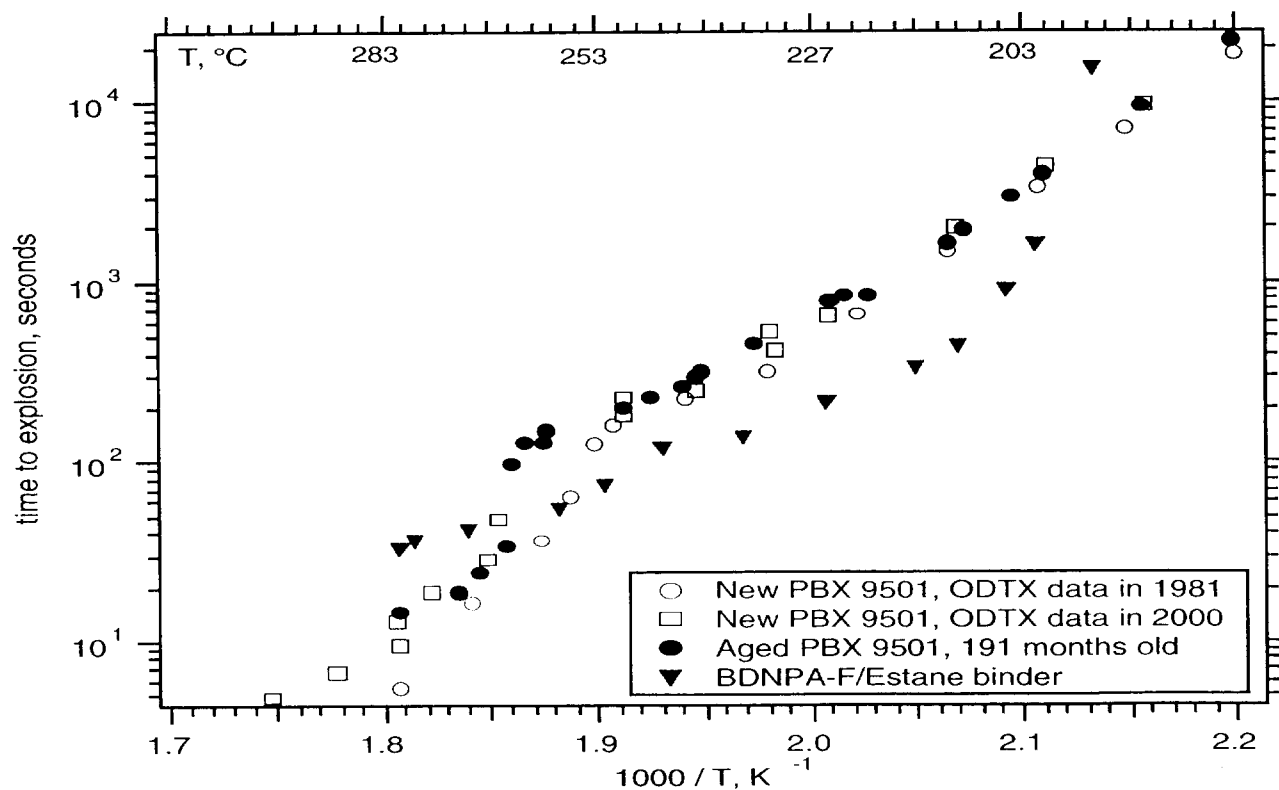


Figure 2. Time to explosion for new and aged PBX 9501, and Estane/BDNPA-F binder specimens. Pure Estane spheres were not reactive with temperatures as high as $300^{\circ}C$.

most of the samples being consumed. The volume increases tend to be scattered but the results did not show any obvious difference in the violence of the thermal responses of new or aged materials. We will report the data in another publication (6).

Kinetic models for HMX-based PBX composites - Thermal decomposition kinetic models have been reported for HMX-containing formulations. We now have pure HMX data to modify these models. The decomposition of HMX is modeled as a 4-step process (3,6). The mechanism for the decomposition of HMX (4 steps), BDNPA-F (2 steps) and Estane (one-step) is shown below.

HMX b → d phase transition (1)

HMX thermal decomposition (3 steps)

$\text{HMX} \rightarrow \text{CH}_2\text{NNO}_2$ (2)

$\text{CH}_2\text{NNO}_2 \rightarrow \text{CH}_2\text{O}, \text{N}_2\text{O}, \text{HCN}, \text{HNO}_2$ (3)

$\text{CH}_2\text{O}, \text{N}_2\text{O}, \text{HCN}, \text{HNO}_2 \rightarrow \text{N}_2, \text{H}_2\text{O}, \text{CO}, \text{CO}_2$ (4)

BDNPA/F thermal decomposition (2 steps)

$\text{BDNPA/F} \rightarrow \text{intermediates}$ (5)

$\text{Intermediates} \rightarrow \text{N}_2, \text{H}_2\text{O}, \text{CO}, \text{CO}_2$ (6)

Estane thermal decomposition (one step)

$\text{Estane} \rightarrow \text{products}$ (7)

This new HMX model includes the beta-to-delta solid phase transition kinetics (3). This phase change is treated separately from the other endothermic processes that precede the exothermic decomposition. Arrhenius kinetics are used for these reactions.

Since the surveillance data for LX-04 showed no change in the composition with aging and the explosion times for new and aged materials are comparable, the same kinetic model is used for both composites. The calculated times to explosion are in good agreement with the experimental values over most of the temperature ranges. Since Viton A is not reactive thermally, it is treated as an endothermic process in the model. The results are reported elsewhere (6). Similarly, the modified HMX model fits the data for HMX well (6).

Figure 3 compares the calculated and experimental data for PBX 9501 and its binder. The calculated explosion times fit the experimental data reasonably well up to about 250°C. The steeper slope at higher temperatures reflects faster decomposition associated with a more complex kinetics in this thermal diffusion-limited region. Differential Scanning Calorimetry (DSC) studies typically showed an exothermic peak above 250°C for HMX-based compounds, indicating auto-ignition conditions. This obviously leads to faster decomposition.

The model for aged PBX 9501 is not as straightforward. Factors that affect its thermal decomposition kinetics are not well understood. One approach was to assume a complete loss (migration) of the BDNPA-F component in the composite. In this scenario, this thermally active constituent (see Figure 2) contributes no exothermic energy to the reaction and thus delays the onset reaction temperature. The calculated data for such 'aged' PBX 9501 (without 2.5 wt% BDNPA-F) fits the experimental results relatively well. While the good agreement between the calculated values and experimental data may have been coincidental, the current model represents the thermal stability limit resulting from one aging mechanism of PBX 9501. Under this scenario, the materials is more thermally stable. Experiments are needed to elucidate the various parameters that may influence the material thermal chemistry.

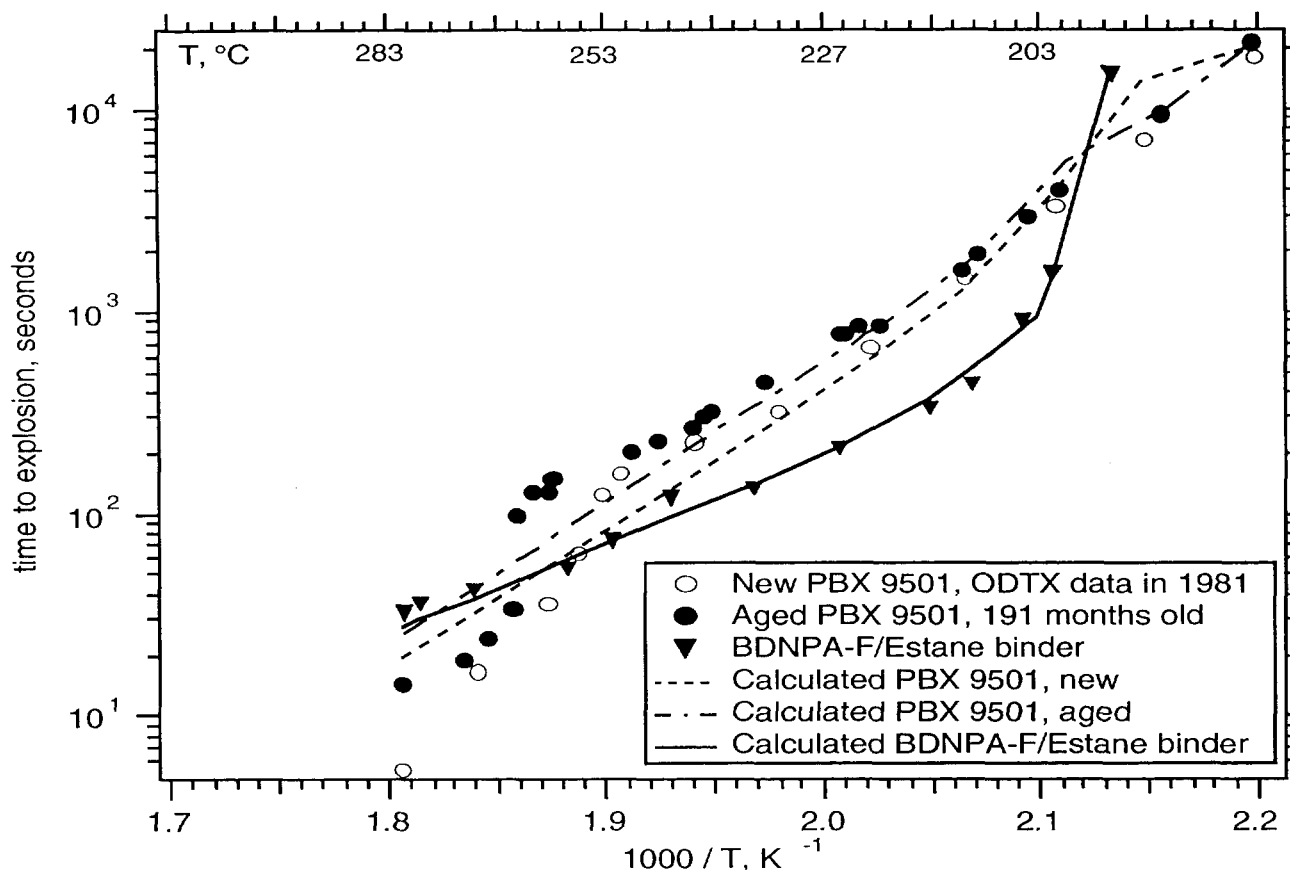


Figure 3. Comparison of the experimental and theoretical treatment of the time to explosion of new and aged PBX 9501 and its binder.

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